# Tunable far-infrared laser spectroscopy of deuterated isotopomers of Ar–$H_2O$

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Molecular descriptions of macroscopic ensembles depend critically on the accuracy with which the various intermolecular forces involved are described. The intermolecular potential energy surface (IPS) is, in general, the key to the understanding of intermolecular forces. Because of this, small, weakly bound clusters have become the subject of intense interest due to their "simple" nature and their impact on the structure and chemistry of aqueous environments, most notably biological systems.[1–4] Indeed, there have been a number of studies in the far-infrared (FIR) and infrared which bear directly on these issues by sampling vibration–rotation-tunneling (VRT) modes intimately associated with the IPS [Ar–HCl, $(HCl)_2$, $(H_2O)_2$, etc.[5–7]], but it is only for atom–diatom adducts that quantitative IPS exist. Recently, however, Cohen *et al.*[8] and Lascola *et al.*[9] have recorded FIR and IR spectra of Ar–$H_2O$, perhaps the simplest example of important "hydrophobic" interactions. Further, Cohen and Saykally[10] have presented an exciting extension of the collocation method as implemented by Peet and Yang[11] to the Ar–$H_2O$ complex, resulting in an accurate IPS, free from dynamical approximations, which they label AW1. This atom–polyatom IPS, inverted directly from the FIR data, is based nearly entirely on VRT states in the ortho levels of $H_2O$; only the van der Waals stretching transition has been reported within the para state. We present here FIR data for Ar–$D_2O$ and Ar–DOH which complement those of Cohen *et al.*,[8] and which should provide exacting tests of the AW1 potential in that they access states not yet detected, and in some cases not connected by symmetry, in the $H_2O$ (or $D_2O$) complex.

Sub-doppler spectra have been obtained for Ar–$D_2O$ and Ar–DOH in the 490–720 GHz range using the tunable FIR laser sideband/planar supersonic jet spectrometer at Caltech. The experimental apparatus used is similar to that used by the Berkeley group,[7,8] and will be reported in detail elsewhere.[12] Formic acid lasers at 584.4 and 693.0 GHz have been used in this study. Gas mixtures of Ar and $H_2O/D_2O/$DOH were prepared by passing Ar gas over a 50/50 mixture of $H_2O$ and $D_2O$ at room temperature. A total of 179 lines were found, of which 110 are assigned to Ar–DOH or Ar–$D_2O$, and 69 are unassigned. Lines due to $H_2O/D_2O$ monomers and dimers were removed by chemistry tests, while those due to Ar–$H_2O$ were removed based on assignments made by Cohen *et al.*[8] Ar–DOH and Ar–$D_2O$ transitions were assigned on the basis of ground-state microwave data and combination differences[13] (and by using pure $D_2O$). A complete listing of the observed transition frequencies is available as supplementary material from the AIP Physics Auxiliary Publication Service (PAPS).[14]

The transitions observed (solid arrows) as well as Coriolis interactions (double-headed arrows) are shown in Fig. 1, whose notation follows that of Cohen *et al.*[8] For Ar–$D_2O$, two distinct bands at 579.7 and 619.6 GHz were observed. The *P*, *Q*, and *R* branches lying at lower energy arise from the $\Sigma^+(0_{00}) \rightarrow \Pi^{\pm}(1_{11})$ transition. The other set of *P* and *R* branches do not possess an associated *Q* branch, and are due to the $\Sigma^+(0_{00}) \rightarrow \Sigma^+(1_{11})$ levels. All these transitions lie within the $D_2O$ para manifold ($n_{\text{stretch}} = 0$). For Ar–DOH, *P* and *R* branches from the $\Sigma^+(0_{00}) \rightarrow \Pi^+(1_{01})$ transition have been detected, along with *Q* branch lines from the $\Sigma^+(0_{00}) \rightarrow \Pi^-(1_{01})$ levels. The Coriolis coupled states are $\Sigma^+(0_{00}) \Leftrightarrow \Pi^+(1_{11})$ for Ar–$D_2O$, and $\Sigma^+(1_{01}) \Leftrightarrow \Pi^+(1_{01})$ for Ar–DOH. As was done in previous FIR studies of Ar–$H_2O$,[8] the transitions were fit to the following Hamiltonian:

$$H(\Sigma) = \nu + B(J(J+1)) - D(J(J+1))^2 + H(J(J+1))^3 + L(J(J+1))^4 + \cdots,$$

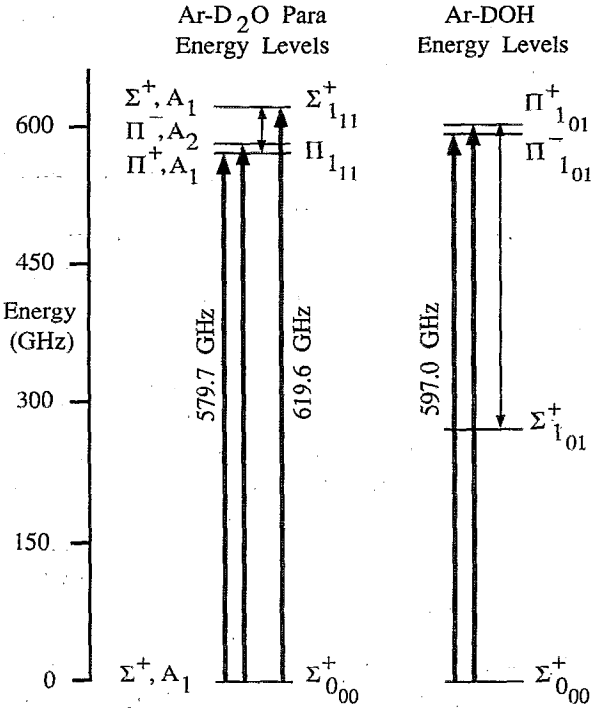


FIG. 1. Energy level diagram and observed transitions for the para levels of Ar–$D_2O$ and for the HDO rotor $1_{01}$ levels of Ar–DOH. Coriolis coupled states are indicated by the double-headed arrows.

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TABLE I. Fitted spectroscopic constants (MHz) for Ar–$D_2O$ and Ar–DOH. Errors are 1 standard deviation of the fit.

| Constants | $\Sigma^+(0_{00})$ | Ar–$D_2O$ $\Sigma^+(1_{11})$ | $\Pi^+(1_{11})$ | $\Pi^-(1_{11})$ |
|---|---|---|---|---|
| $\nu$ | 0.0(fixed)[a] | 619 643.47(34) | 579 652.75(32) | 579 652.75(32) |
| $B$ | 2795.93(fixed)[a] | 2808.409(30) | 2793.526(22) | 2793.526(22) |
| $D$ | 0.078137(fixed)[a] | 0.136 24(85) | 0.013 84(74) | 0.079 06(33) |
| $H$ | −2.406$E$-6(fixed)[a] | −2.33(69)$E$-5 | −1.49(58)$E$-6 | −1.7(1.3)$E$-6 |
| $L$ | ··· | −0.84(18)$E$-7 | 1.40(14)$E$-7 | ··· |
| $\beta$ | | | 5141.09(12) | |

| Constants | $\Sigma^+(0_{00})$ | Ar–DOH $\Sigma^+(1_{01})$ | $\Pi^+(1_{01})$ | $\Pi^-(1_{01})$ |
|---|---|---|---|---|
| $\nu$ | 0.0(fixed)[a] | 270 336.6[b] (fixed) | 597 037.51(28) | 597 037.51(28) |
| $B$ | 2889.919(42) | 2880.0[c] (fixed) | 2856.472(37) | 2856.472(37) |
| $D$ | 0.0873 22(64) | 0.0[c] (fixed) | 0.123 73(54) | 0.107 67(60) |
| $H$ | −8.8(3.0)$E$-6 | 0.0[c] (fixed) | −2.65(22)$E$-5 | ··· |
| $\beta$ | | | 5414.55(60) | |

[a] These values were determined from microwave data on the ground state.
[b] This value is that predicted by fits to near-IR and FIR data (Ref. 14).
[c] These values were estimated by analogy with Ar–$H_2O$.

$$H(\Pi) = \nu + B(J(J+1) - l^2) - D(J(J+1) - l^2)^2 + H(J(J+1) - l^2)^3 + \cdots,$$

$$H_{\text{Coriolis}} = \beta(J(J+1))^{1/2},$$

where $H_{\text{Coriolis}}$ couples the $\Sigma^+$ to the $\Pi^+$ state (as shown in Fig. 1). For Ar–$D_2O$, the constants were fit simultaneously, forcing $\nu$ and $B$ for $\Pi^+$ and $\Pi^-$ to be the same and allowing $D$, $H$, $L$ to vary. For the Ar–DOH spectrum, where $\Sigma^+(0_{00}) \rightarrow \Sigma^+(1_{01})$ was not observed, we have used predicted values to estimate the $\Sigma^+(1_{01})$ energy.[15] The results are summarized in Table I. In order to estimate the effect of errors in the location of the $\Sigma^+(1_{01})$ state on $\beta$, values $\pm 1$ $cm^{-1}$ from that predicted were substituted and the parameters adjusted to fit the observed line frequencies. The Coriolis coupled constants obtained for each value of $\nu(\Sigma^+(0_{00}) \rightarrow \Sigma^+(1_{01}))$ are 5662.35(62), 5414.55(59), and 5160.76(56) MHz for $\nu = 8$, 9.06, and 10 $cm^{-1}$. Adopting the error of 0.1 $cm^{-1}$ predicted theoretically,[14] $\beta$ can be determined to about $\pm 25$ MHz. We note that our measured $\Pi$ state locations are in nearly quantitative agreement with the predictions of the AW1 potential, while the measured $\Sigma$ state energies are roughly 0.6–0.7 $cm^{-1}$ above that predicted.[16]

To summarize, we have measured several far-infrared VRT transitions in deuterated isotopomers of Ar–$H_2O$ for the first time; namely the $\Sigma^+(0_{00}) \rightarrow \Sigma^+(1_{11})$ and $\Sigma^+(0_{00}) \rightarrow \Pi^{\pm}(1_{11})$ transitions for Ar–$D_2O$, and the $\Sigma^+(0_{00}) \rightarrow \Pi^{\pm}(1_{01})$ transitions for Ar–DOH. These experimental results will enable the generation of improved multidimensional potential energy surfaces for the Ar–$H_2O$ system when combined with existing microwave, far-infrared, and infrared data. The $\Sigma^+(0_{00}) \rightarrow \Pi^{\pm}(1_{01})$ constants for Ar–DOH should prove particularly valuable since symmetry forbids transitions between these levels in the Ar–$D_2O$ and Ar–$H_2O$ complexes.

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[1] D. C. Rapoport and H. A. Scheraga, J. Phys. Chem. **86**, 873 (1982).
[2] K. Watanabe and H. C. Andersen, J. Phys. Chem. **90**, 795 (1986).
[3] L. R. Pratt and D. C. Chandler, J. Chem. Phys. **73**, 3434 (1980).
[4] A. Ben-Naim, J. Chem. Phys. **90**, 7412 (1989).
[5] R. Robinson, D. H. Gwo, and R. J. Saykally, J. Chem. Phys. **87**, 5156 (1987); Mol. Phys. **63**, 1021 (1988); J. M. Hutson, J. Chem. Phys. **91**, 4448 (1989).
[6] M. D. Schuder, C. M. Lovejoy, D. D. Nelson, Jr., and D. J. Nesbitt, J. Chem. Phys. **91**, 4418 (1989); G. A. Blake and R. E. Bumgarner, J. Chem. Phys. **91**, 7300 (1989).
[7] K. L. Busarow, R. C. Cohen, G. A. Blake, K. B. Laughlin, Y. T. Lee, and R. J. Saykally, J. Chem. Phys. **90**, 3937 (1989); Z. S. Huang and R. E. Miller, *ibid.* **91**, 6613 (1989).
[8] R. C. Cohen, K. L. Busarow, K. B. Laughlin, G. A. Blake, M. Havenith, Y. T. Lee, and R. J. Saykally, J. Chem. Phys. **89**, 4494 (1988); R. C. Cohen, K. L. Busarow, Y. T. Lee, and R. J. Saykally, *ibid.* **92**, 169 (1990).
[9] R. Lascola, C. M. Lovejoy, and D. J. Nesbitt, 45th Ohio State University Symposium on Molecular Spectroscopy, Abstract TA2, 74 (1990).
[10] R. C. Cohen and R. J. Saykally, J. Phys. Chem. (in press).
[11] A. C. Peet and W. Yang, J. Chem. Phys. **91**, 6598 (1989).
[12] G. A. Blake, R. E. Bumgarner, and J. Lai (in preparation).
[13] G. T. Fraser, F. J. Lovas, R. D. Suenram, and K. Matsumura, J. Chem. Phys. (in press).
[14] See AIP document no. PAPS JCPSA-94-824-2 for 2 pages of the complete listing of the observed transition frequencies. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, NY 10017. The price is $1.50 for each microfiche (98 pages) or $5.00 for photocopies of up to 30 pages, and $0.15 for each additional page over 30 pages. Airmail additional. Make checks payable to the American Institute of Physics.
[15] Private communication with C. M. Lovejoy.
[16] Private communication with R. C. Cohen.